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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the hydrogen-peroxide system penetrant remover used for washing of a silicon wafer and a semiconductor device. In more detail, surface tension of this invention is low, and its contact angle to a silicon wafer front face is small, it is excellent in wettability, and relates to the hydrogen-peroxide system penetrant remover which can be used suitable for washing of the high integrated-semiconductor element of a detailed pattern, and washing of a silicon wafer.

[0002]

[Description of the Prior Art] The degree of integration of a semiconductor device improves every year, and manufacture of 4MDRAMs is possible for it now. In connection with this, a pattern becomes still more detailed and line breadth is also 1 micrometer. It is becoming the following. In order to perform washing or etching of such a detailed pattern effectively, the processing liquid an invasion in the gap of a detailed pattern is easy low surface tension, and the contact angle exceeded [ liquid ] in wettability small is needed.

[0003] A surfactant is effective in generally raising wettability, a semiconductor device is processed or the method of using the processing liquid which added the surfactant in the solution of a surfactant beforehand is used. For example, in the case of the buffered fluoric acid (mixed liquor of fluoric acid and an ammonium fluoride) used for etching of a silicon oxide, use (JP,63-283028,A ) of use (JP,60-39176,A ) of a \*\* fluorine carboxylic acid, use (JP,60-249332,A ) of fluoro alkyl sulfonate, an aliphatic carboxylic acid or a salt, a fatty amine, and fatty alcohol etc. is proposed as an effective surfactant.

[0004] On the other hand, since the penetrant remover of a hydrogen-peroxide system is effective in washing of dust, a metal impurity, etc., it is widely used for washing of a silicon wafer and a semiconductor device, and the acid penetrant remover combined with acids, such as a hydrochloric acid, a formic acid, a sulfuric acid, and fluoric acid, and the alkaline penetrant remover combined with alkali, such as aqueous ammonia, a choline (hydro KISHIRU trimethylammonium hydroxide), and TMAH (tetramethylammonium hydroxide), are used. When washing a semiconductor device using a hydrogen-peroxide system penetrant remover, the penetrant remover which improved similarly is demanded. Moreover, a hydrogen-peroxide system penetrant remover which is excellent in wettability also in washing of a silicon wafer, and can remove efficiently the dust on the front face of a silicon wafer is desired. Furthermore, when an alkaline hydrogen-peroxide system penetrant remover washes a silicon wafer, generating of this detailed irregularity is posing a problem in the latest high integration and thin-film-izing of the oxide film accompanying it that it is easy to produce detailed irregularity on a silicon wafer front face. Development of the hydrogen-peroxide system penetrant remover which shows the leveling effect and may raise surface smooth nature from this point is desired strongly.

[0005] By the way, a surfactant is used for generally improving wettability. However, the surfactant which fitted the penetrant remover of a hydrogen-peroxide system truly was not what also satisfies surfactants, such as an alkylbenzene sulfonic acid currently conventionally used together with the hydrogen peroxide by the bleaching agent etc., as well as a \*\* fluorine carboxylic acid, fatty alcohol, etc. which are not yet found out, for example, are proposed by buffered fluoric acid according to examination of this invention persons.

[0006]

[Problem(s) to be Solved by the Invention] While this invention persons looked for the surfactant suitable for the hydrogen-peroxide system penetrant remover used for the basis of the above-mentioned background by washing of a silicon wafer and a semiconductor device etc., as a result of performing still more detailed condition examination, it became clear that the surfactant which can be used for this invention needs to fulfill the following conditions.

\*\* Addition of a surfactant is taking effect with the little addition of 500 ppm or less which can disregard foaming, since foaming of a penetrant remover is generated and it becomes the obstacle of washing.

\*\* In order to show an effect with practical addition of a surfactant, the surface tension under a service condition is [ dyne / 30 //cm ]. The contact angle to a hydrophobic silicon front face needs to be 5 or less times further in below.

\*\* Washing is comparatively performed often near 85 degree C at an elevated temperature, and an effect must not be lost at an elevated temperature.

\*\* Since degradation of a surfactant is large with especially the mixed liquor of aqueous ammonia/hydrogen peroxide, it must be stable in the mixed liquor of aqueous ammonia/hydrogen peroxide.

\*\* After manufacture, although a penetrant remover performs dust removal by cycle filtration, it is removed in this process and

must not lose an effect.

[0007] It is in offering the hydrogen-peroxide system penetrant remover which can wash the semiconductor device of high accumulation effectively that a contact angle [ as opposed to / satisfy each / of the above / the purpose of this invention ] conditions, and surface tension is low, and / a silicon front face / is small, and it is easy to go into the gap of a detailed pattern, is excellent in wettability, and can be used removal of dust and a cleaning effect are high and suitable also for washing of a silicon wafer.

[0008]

[Means for Solving the Problem] As a result of looking for the surfactant with which are satisfied of the above-mentioned conditions, this invention persons find out that a certain kind of ethyleneoxide addition type non-ion system surfactant is specifically effective, and came to complete this invention. That is, this invention relates to the acid or alkaline hydrogen-peroxide system penetrant remover containing the hydrogen peroxide beyond 1wt% at the silicon wafer and semiconductor device penetrant remover which are characterized by adding 5-500 ppm of ethyleneoxide addition type non-ion system surfactants whose numbers of addition mols of an ethyleneoxide are 3-10.

[0009] As an example of representation of the ethyleneoxide addition type non-ion system surfactant used by this invention, three sorts, polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, and polyoxyethylene fatty acid ester, are raised. Although the carbon number of an alkyl group and a fatty acid will not be limited here especially if the effect as a lipophilic group of a surfactant is shown, generally a carbon number, and 4-22 are suitable.

[0010] On the other hand, the length of a polyoxyethylene chain, i.e., the number of addition mols of an ethyleneoxide, is one of the requirements important as a surfactant used for this invention, and this number of addition mols needs to be in the range of 3-10. If there are few addition mols of an ethyleneoxide than 3, the reduction effect of sufficient surface tension and a contact angle will not be acquired. On the contrary, although effect is taken in early stages when there are more addition mols than 10, in washing conditions which are especially heated at 85 degrees C by ammonia / hydrogen-peroxide system penetrant remover, degradation is large, the effect cannot be maintained but use is substantially difficult. Moreover, the addition of a surfactant is also important in this invention, and it is necessary to stop at least 500 ppm or less in addition of 100 ppm or less desirably from the above-mentioned washing in this invention used for washing of a silicon wafer and a semiconductor device. Moreover, 5 ppm In the following cases, the desired end of this invention is not attained.

[0011] Although more than 1wt% is required for the hydrogen-peroxide concentration of the hydrogen-peroxide system penetrant remover by which the surfactant of this invention is added, generally 3 - 30wt% concentration is used suitably. Moreover, in order for the penetrant remover of a hydrogen-peroxide system to show a cleaning effect, an acid or alkali needs to be added, and alkali, such as aqueous ammonia, a choline, and TMAH, is mainly added by removal of a metal impurity at the purpose of the dust removal [ a hydrochloric acid a formic acid, fluoric acid, etc. ] of a sulfuric acid to removal of organic impurities. Although the addition of these acids or alkali is suitably determined according to the purpose and it is not limited especially, generally it is added by the concentration beyond 0.1wt%. The usual addition method is sufficient, and it may add beforehand to a hydrogen peroxide, an acid, alkali, or a dilution water, and after preparing a penetrant remover, addition of a surfactant does not interfere, even if it adds at the last. Next, an example explains this invention concretely.

[0012]

[Example 1] A hydrogen peroxide, 28% aqueous ammonia, and ultrapure water were mixed in proportion of 4:1:20 (capacity factor) 31%, 100 ppm of field side activators shown in Table 1 were added to this, respectively, and the penetrant remover was adjusted to it. The surface tension and the contact angle of this penetrant remover were measured at 30 degrees C and 85 degrees C. Furthermore, about surface tension, it measured again at 30 degrees C after cooling the liquid measured at 85 degrees C, and the degree of degradation by 85-degree-C heating was judged. In addition, measurement of surface tension used the automatic surface tension balance CBVP-Amade from Consonance Interface Science 3 type (UIRU helmet I formula). Moreover, the contact angle meter CA-D type made from Consonance Interface Science (sessile drop method) was used for measurement of a contact angle, and the contact angle to a hydrophobic silicon front face was measured using the silicon wafer from which the scaling film was removed by rare fluoric acid processing. Under the present circumstances, measurement at 30 degrees C was performed in 180 seconds after the bottom of a drop, and since measurement at 85 degrees C had quick evaporation of liquid, it was performed after 10 seconds.

[0013]

[Table 1]

表面張力及び接触角

界面活性剤	表面張力 (dyne/cm)			劣化	接触角 (度)		備考
	30°C	85°C	30°C (再)		判定	30°C	
ポリオキシエチレン ラクリルエ - テル (商品名エマルゲン 147)	41	47	50	X	11	9	エチレンオキサイド 付加モル数47
同上	37	44	45	X	7	6	20
同上	27	26	28	O	<5	<5	6
同上	27	26	28	O	<5	<5	5
ラクリルアルコ - ル エニスエ - テル (商品名エマルゲン 106)	27	64	41	X	50	53	0
ポリオキシエチレンアルキル ラクリルエ - テル (商品名エマルゲン 905)	30	27	29	O	<5	<5	エチレンオキサイド 付加モル数 5
同上	41	44	47	X	9	6	20
(商品名エマルゲン 920)							

[0014]

[Example 2] It replaced with the mixed liquor which mixed the penetrant remover of an example 1 to the hydrogen peroxide and 36% hydrochloric acid 31%, and mixed ultrapure water in proportion of 1:1:6 (capacity factor), the same experiment was conducted, and the effect of a surfactant was investigated. This is shown in Table 2. (Following margin)

[0015]

Table 2 Surface tension and contact angle measurement result Surfactant Surface tension (dyne/cm) Contact angle (degree) Note 30 degree-C 85 \*\* 30 \*\* (\*\*) 30 \*\* 85 \*\* ----- Polyethylene GURIKO - RU 27 27 28 <5 <5 30 degree-C 85 \*\* 30 \*\* (\*\*) 30 \*\* 85 \*\* ----- Ethyleneoxide RAURIRUE - Tell The number of addition mols Six (tradename emulgen 106) Nothing (100 ppm addition) 71 6270 60 It was admitted that the surfactant of 58 this inventions was effective also in an acid hydrogen-peroxide system cleaning agent.

[0016]

[Example 3] Emulgen 106 of an example 1 About the penetrant remover which added 100 ppm, it is 0.2. mum The influence of filtration with a Teflon filter was investigated. A result is shown in Table 3.

[0017]

table 3 Surface tension (dyne/cm) Contact angle (degree) Before filtration 27 26 <5 <5 After filtration 28 26 <5 <5 It was 30 degrees C 85 \*\* 30 \*\* 85 \*\* ----- admitted that the surfactant of this invention did not lose an effect by filter filtration, either.

[0018]

[Example 3] It is 0.5 micrometers about the 3 inches silicon wafer from which the natural oxidation film was removed by rare fluoric acid processing. The silicon wafer which it was immersed [ silicon wafer ] in the solution which distributed the polystyrene latex particle, and made the particle adhere on a wafer was immersed in the penetrant remover of an example 1 for 5 minutes at

85 degrees C, and the removal effect of a particle was investigated. Moreover, the experiment with the same said of the penetrant remover which does not add a surfactant from the penetrant remover of an example 1 as comparison was conducted. In addition, scanning-electron-microscope observation performed measurement of the adhesion particle number on a wafer.

[0019] table 4 The adhesion particle number on a wafer (piece/cm<sup>2</sup>) Elimination factor (%) A surfactant Before washing After washing

Existence of addition \*\* 221 2 99 Nothing 206 19 91. [0020]

[Effect of the Invention] As above, since surface tension is low and the contact angle to a silicon front face is small, the penetrant remover of the hydrogen-peroxide system which added the surfactant of this invention can wash the semiconductor device of high accumulation effectively that it is easy to go into the gap of a detailed pattern. Moreover, it excels in wettability and the cleaning effect of dust can use it it is high and suitable also for washing of a silicon wafer.

(表1 続き)

界面活性剤	表面張力(dyne/cm)			劣化	接触角(度)		備考
	30°C	85°C	30°C(再)		判定	30°C	
ブリオキシチレン モノオレート	30	29	30	○	<5	<5	エチレンオキサイド 付加モル数10 (商品名エマーン 4110)
ソルビタンモノオレート	30	40	52	×	48	27	
ソルビタントリオレート	32	41	42	×	50	37	(商品名レオ - ■ SPO-10)
オクチルドекан酸	63	62	69	×	42	36	
ベラルゴン酸	67	63	69	×	37	36	
パーカルオロアルキカルボン酸	29	61	62	×	34	25	(商品名 フローラ FC129)
アルキルベンゼンスルホン酸	28	52	43	×	<5	6	(商品名 ライポン LH-200)
アセチル酸エステル	29	55	47	×	42	27	(商品名 エレカット M)
なし(無添加)	71	65	71		51	58	

上記の表から、30°C、85°Cいずれにおいても表面張力30 dyne/cm 以下、接触角5度以下であり、かつ劣化の少ない界面活性剤はエチレンオキサイド付加モル数が3~10の非イオン系界面活性剤のみであることが認められる。

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CLAIMS

[Claim(s)]

[Claim 1] The silicon wafer and semiconductor device penetrant remover which are characterized by adding 5-500 ppm of ethyleneoxide addition type non-ion system surfactants whose numbers of addition mols of an ethyleneoxide are 3-10 to the acid or alkaline hydrogen-peroxide system penetrant remover containing the hydrogen peroxide beyond 1wt%.

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(19)



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(54) CLEANING SOLUTION FOR SILICON WAFER  
AND SEMICONDUCTOR DEVICE

(57) Abstract:

PURPOSE: To provide a cleaning method of a silicon wafer which demonstrates excellent wettability, high dust removal, and high cleaning effect, by adding a specific non-ionic surface active agent to an acidic or alkaline hydrogen peroxide cleaning solution.

CONSTITUTION: A cleaning solution for silicon wafers and semiconductor devices is yielded by adding a 5-500ppm ethylene oxide-added non-ionic surface active agent where the number of mols of added ethylene oxide is 3-10 into a hydrogen peroxide cleaning solution containing 1% by

weight or more hydrogen oxide added non-ionic surface active agent involve polyoxyethylene alkyl ether, poloxyethylene ether, and poloxyethylene fatty ester. The cleaning solution is likely to enter gaps of a fine pattern and has a high dust cleaning effect.

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